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Quantum Confinement Effects in Self-assembled Multicomponent Semiconducting Polymers

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Abstract

Semiconducting polymer heterostructures exhibiting quantum confinement effects were recently prepared in our laboratory by a self-assembly approach. Photoluminescence and photoluminescence excitation spectroscopies as well as electric field-induced photoluminescence quenching have been used here to probe the effects of exciton confinement in the self-assembled semiconducting polymer quantum-well nanostructures.

Keywords: self-organization in macromolecules; quantum wells; photoluminescence; other conjugated polymers; semiconductor-semiconductor heterostructures; light sources.

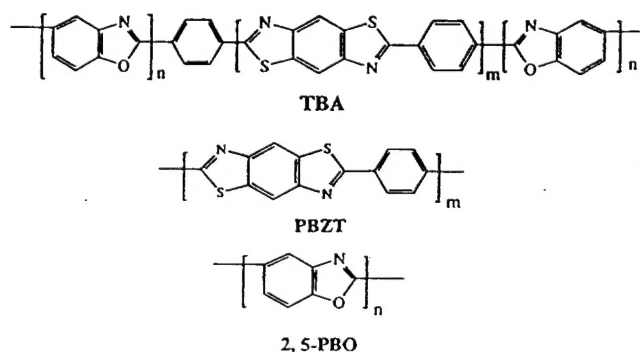
Introduction

Intense research efforts on inorganic semiconductor nanostructures and heterostructures, such as multiple quantum wells (MQWs), superlattices (SLs), quantum (well) wires (QWWs) and quantum boxes (QBs), have resulted in discovery of novel phenomena and properties in semiconductors and the fabrication of more efficient electronic and optoelectronic devices [1-4]. The expectation of realizing similar novel electronic and optical effects and improved properties of organic materials has motivated research interest on low dimensional organic semiconductors in the past 10 years [5-12]. Extensive theoretical studies of block conjugated copolymers, such as triblock $A_nB_mA_n$ and multiblock $(-A_nB_y-)_n$ heterostructures, have demonstrated the theoretical possibility of achieving MQWs, SLs, and their associated quantum confinement effects in semiconducting polymers [5,6]. However, the few prior experimental attempts to synthesize such block copolymers did not produce materials with evidence of quantum effects [7,8]. Other approaches to semiconducting polymer nanostructures, such as sequential electrochemical polymerization, have also not led to experimental demonstration of quantum effects [12].

Organic molecular beam deposition (OMBD) technique, which is similar to ultrahigh vacuum molecular beam epitaxy (MBE) that is widely used to prepare inorganic MQWs and SLs, was recently successfully used to grow layered organic multiple quantum wells from naphthalene and perylene derivatives [9,10]. Excitons in these OMBD-grown layered heterostructures have been shown to behave as a two-dimensional system with strong confinement in one direction [9]. Although exciton confinement and quantum size effects were demonstrated, the characteristic discrete excitonic features in absorption or excitation spectra commonly observed in inorganic semiconductor MQWs and SLs [2-4] were not observed in the organic MQWs [9,10].

Very recently, we reported a novel self-assembly approach to preparing semiconducting polymer quantum boxes and quantum

wires and the first experimental observation of the discrete exciton states in a low dimensional organic semiconductor [11b]. Here, we briefly discuss aspects of quantum confinement of excitons in these novel self-assembled semiconducting polymer heterostructures. Quantum boxes and wires investigated here were prepared from the semiconducting homopolymers poly(benzobisthiazole-1,4-phenylene)(PBZT) and poly(2,5-benzoxazole)(2,5-PBO) and triblock copolymer poly(2,5-benzoxazole)-*block*-poly(benzobisthiazole-1,4-phenylene)-*block*-poly(2,5-benzoxazole) which is denoted TBA [11]:



The symmetric $A_nB_mA_n$ triblock copolymer TBA has a middle PBZT block and two outer 2,5-PBO blocks. The homopolymers PBZT and 2,5-PBO have energy gaps, based on absorption band edges, of 2.48 eV and 3.24 eV, respectively [11]. Thus, the PBZT block of TBA represents a quantum well and the 2,5-PBO blocks constitute electron potential barriers with a height of $\Delta E_g = E_g^A - E_g^B = 0.76$ eV. However, the *as-synthesized* triblock copolymer was shown to be

microphase separated with consequent aggregation of PBZT block chains [11]. By blending a triblock copolymer with the higher energy-gap homopolymer (2,5-PBO), self-assembled semiconducting polymer heterostructures are obtained in which isolated single chains of the triblock can be obtained. If the block length of the PBZT in TBA is small (2-9 repeat units), quantum boxes could be obtained when compared to the exciton Bohr radius (a_0) of PBZT ($a_0 = 13 \text{ \AA}$) [13]. On the other hand, PBZT repeat units of 15 or more in TBA ensures that a quantum wire could be obtained. The repeat unit lengths of PBZT and 2,5-PBO are 12.5 and 11.6 \AA , respectively, from their X-ray data.

Experimental Section

The detailed synthesis and characterization of the materials (TBA, 2,5-PBO, and PBZT) and the self-assembly approach to preparing the semiconducting polymer quantum wires and boxes have been described elsewhere [11,14]. The particular triblocks discussed here are $A_{20}B_6A_{20}$ (TBA-1), $A_{25}B_6A_{25}$ (TBA-2), and $A_{20}B_{20}A_{20}$ (TBA-4). Thin films of the triblocks and triblock/2,5-PBO blends were obtained by spin coating of their solutions in either formic acid/methane sulfonic acid (9:1 by weight) or trifluoroacetic acid onto silica or indium-tin-oxide (ITO) glass substrates. The film thickness was measured by an Alpha Step profilometer which has a resolution of 1 nm. The film thickness was typically in the range of 100-180 nm. Aluminum was evaporated onto samples on ITO glass for electric field-induced photoluminescence (PL) quenching measurements. All photophysical measurements were made by using instrumentation and techniques already described [15,16]. For PL measurements under an external field, a positive bias voltage was applied to the ITO electrode.

Results and Discussion

Figure 1 shows the optical absorption spectrum of the pure TBA-4 thin film. The spectrum consists of a band in the visible (400-490 nm) characteristic of the PBZT block and a band in the UV that corresponds to the absorption of the 2,5-PBO chromophore. Comparison of the TBA-4 absorption spectrum to those of the parent homopolymers (not shown) clearly show that it is a mere superposition of those of the component blocks. No new features are observed in the absorption spectrum of the block copolymer. Also shown in Figure 1 is the room temperature (298K) photoluminescence excitation (PLE) spectrum (monitored at 600 nm where 2,5-PBO does not emit) of TBA-4 blend with 2,5-PBO at a concentration of 0.5 mol% PBZT repeat units which means about 1 TBA-4 chain per 66 chains of 2,5-PBO. The relatively long PBZT block (20 repeat units or 25 nm long) in the 0.5% TBA-4/2,5-PBO blend is completely isolated, forming a *PBZT quantum wire*. The PLE spectrum of isolated TBA-4 chains (Fig.1) clearly shows features corresponding to those in the absorption spectrum of pure TBA-4. However, there are additional new peaks in the PLE spectrum at 505 nm (2.46eV) and 544 nm (2.28eV). These new PLE peaks depend on the concentration of the blend, being absent in the pure triblock and more intense and observable in the dilute blends (0.5 to 5%). These new optical transitions can be assigned to the excitonic states of the PBZT quantum wires. Similar PLE results have been obtained with other triblock copolymer compositions (e.g. TBA-1 and TBA-2) and their blends with 2,5-PBO.

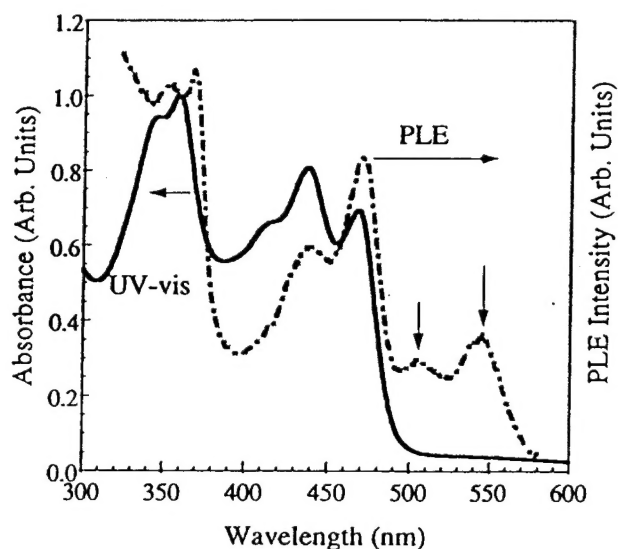


Fig. 1. UV-Vis spectrum of TBA-4 thin film and the 298K PLE spectrum of a 0.5% TBA-4/2,5-PBO blend monitored at 600 nm. New Peaks are indicated by vertical arrows.

The progressive two-dimensional (2-D) spatial confinement of PBZT quantum wires as TBA-4 was diluted in the matrix of 2,5-PBO was also clearly evident in the PL spectra. Figure 2 shows the thin film PL spectra of TBA-4, several blends of TBA-4/2,5-PBO, and the PBZT homopolymer which can be considered as the "bulk" semiconducting polymer. The "bulk" PBZT has a broad featureless PL spectrum that originates from the interchain excimer [15]. Increasing dilution of TBA-4 in 2,5-PBO matrix and hence increasing 2-D confinement of the PBZT quantum wires shows up in the PL spectra as a blue shift from the pure PBZT and band narrowing (Fig.2). In the dilute blends ($\leq 5\%$), the PL spectrum of PBZT quantum wire has little or no Stokes shift ($\sim 2-3 \text{ nm}$). The relative luminescence efficiency of the PBZT quantum wires was factors of up to 4 and 7 enhanced compared to the pure TBA-4 and the pure PBZT homopolymer, respectively.

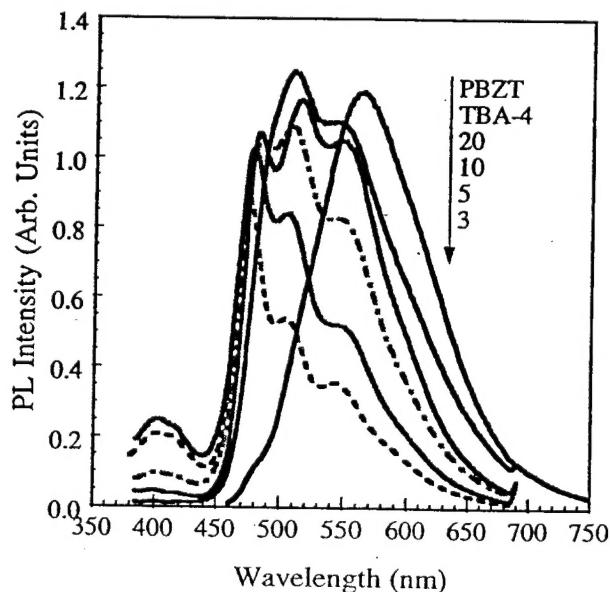


Fig. 2. Thin film PL spectra of pure PBZT (440 nm excitation) and pure TBA-4 and its blends excited at 360 nm. The numbers are in mol.% PBZT repeat units.

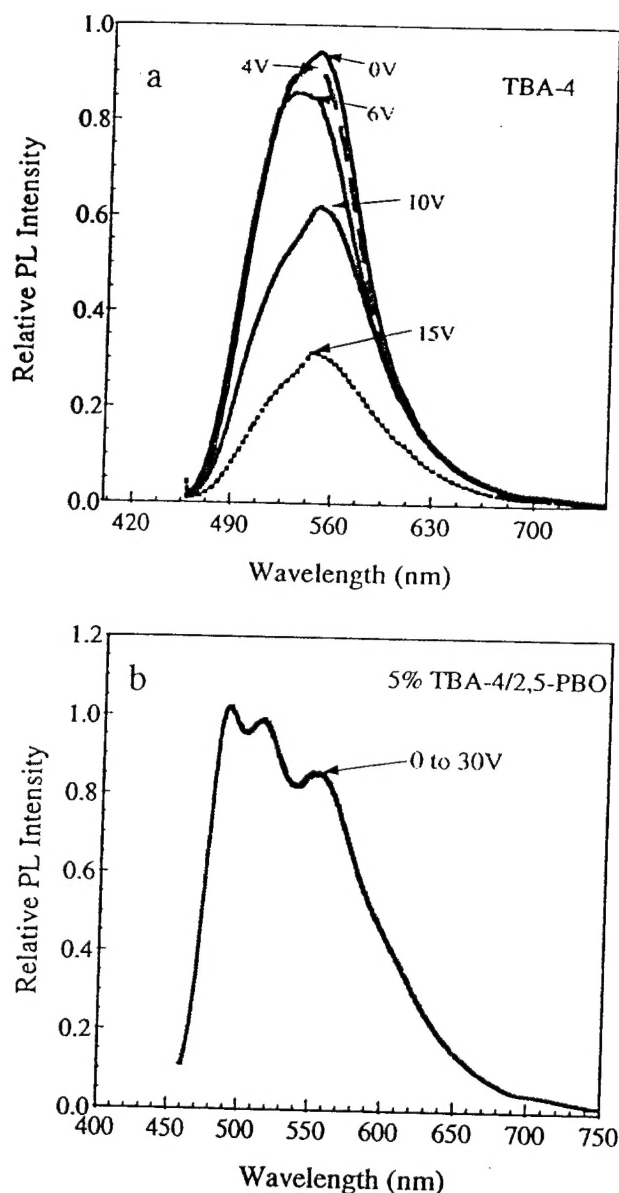


Fig. 3. Electric field-induced PL quenching of TBA-4 (a) and 5% TBA-4/2,5-PBO blend (b) at several applied positive bias voltages. All PL spectra from 435 nm excitation.

Electric field-induced quenching of photoluminescence provided another technique for probing the effects of exciton confinement in quantum wires and boxes. Exciton dissociation into free charge carriers by an applied electric field is an important mechanism of luminescence quenching that is relevant to the application of semiconducting polymers in light-emitting diodes (LEDs) and to the dimensionality of the excitons. In this experiment, thin films of TBA-4 or TBA-4/2,5-PBO blends sandwiched between ITO and aluminum electrodes were photoexcited under positive bias voltages while the PL emission was collected. Our results showed that PL quenching strongly depends on the blend concentration and hence on the exciton confinement dimensionality as well as on the applied field (Figs. 3 and 4). The dramatic PL quenching of pure TBA-4 at different voltages is shown in Figure 3a, reaching intensity reduction of about 70%. In contrast, no PL quenching was observed in the dilute blends (PBZT quantum wires) at bias voltages up to

30V or 3×10^6 V/cm. The strong concentration dependence of field-induced PL quenching is shown in Figure 4 for a field of 10^6 V/cm. These results clearly demonstrate that excitons in semiconducting polymers of reduced dimensionality are more stable under applied fields. Therefore, semiconducting polymer quantum wires and quantum boxes represent one approach to enhancing the electroluminescence efficiency of polymer LEDs. We point out that a recent report on electric field-induced PL quenching of a poly(p-phenylene vinylene) derivative blended with a *nonconjugated* polymer, polycarbonate, reached a somewhat similar conclusion [17]. As noted by those authors, although dilute blends of the conjugated polymer in polycarbonate exhibited the greatest PL stability under applied electric fields, such materials would not be useful for LEDs because of poor charge transport. Because both components in our blends making up the semiconducting polymer quantum wires and boxes investigated here are electroactive and photoactive [11,14,15], they are fundamentally different.

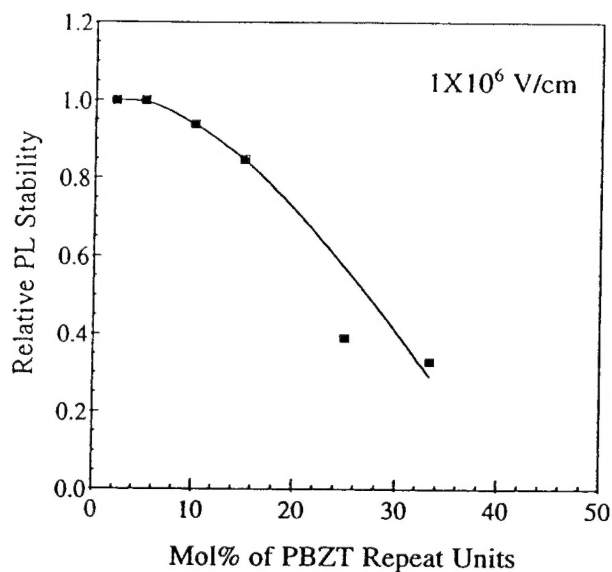


Fig. 4. The relative PL stability as a function of TBA-4/2,5-PBO blend composition (mol.% PBZT repeat units) at a field of 10^6 V/cm.

Conclusions

In summary, we have briefly discussed some aspects of the quantum confinement of excitons in our recently prepared semiconducting polymer wires and quantum boxes [11]. Of fundamental interest is the detection of new discrete exciton states which confirm the low dimensional nature of the excitons in these semiconducting polymer heterostructures. Further studies of such organic semiconductor quantum wires and boxes are warranted and may indeed reveal enhanced properties of device interest as originally envisioned [5-7].

Acknowledgments

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